



## Proton-conducting electrolyte membranes based on organosiloxane network/sulfonated poly(ether ether ketone) interpenetrating polymer networks embedding sulfonated mesoporous benzene–silica



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### HIGHLIGHTS

- SPEEK/OSPN IPN membranes embedding sulfonated mesoporous benzene–silicas (SMBS) were prepared.
- 2D-hexagonal cylindrical mesopore structures of SMBS enhanced the conductivity even at low RH.
- Flexibility and toughness properties of OSPN compensated for the brittleness of the SPEEK membranes.
- Properties of membrane were correlated with ionic cluster dimension measured by SAXS.

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### ABSTRACT

Composite membranes based on organosiloxane network (OSPN)/sulfonated poly(ether ether ketone) (SPEEK) interpenetrating polymer network (IPN) structures with sulfonated mesoporous benzene–silica (SMBS) proton conductors embedded are fabricated. The flexibility and toughness properties of OSPN are expected to compensate for the brittleness of the SPEEK membranes. The 2D-hexagonal cylindrical mesopore structures of SMBS maintain the water content at a high level to enhance the conductivity, even at low relative humidity. Compared to the pristine SPEEK membranes, the ternary composite membranes can endure about 10 times more elongation before breaking. Both OSPN and SMBS components enhance the proton conductivity of SPEEK membranes in a hydrated state, while maintaining the water uptake at below 55% even at temperatures as high as 100 °C. The SAXS patterns of the composite membranes explain the water-related membrane properties of composite membranes. The maximum power densities of Nafion membrane-based MEAs are 178.4 mA cm<sup>-2</sup>, 132.2 mA cm<sup>-2</sup>, and 90.9 mA cm<sup>-2</sup>, but those of composite membrane-based ones are 159.1 mA cm<sup>-2</sup>, 134.2 mA cm<sup>-2</sup>, and 110.8 mA cm<sup>-2</sup> at 95%, 70%, and 45% relative humidity, respectively.

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### 1. Introduction

Polymer electrolyte membrane fuel cells (PEMFCs) are expected to have potential for application in transportation and mobile power sources. Polymeric electrolyte membranes in PEMFC should possess not only environmental stability, but also proton conducting function at relatively mild operating temperatures, compared to other types of fuel cell systems such as molten carbonate fuel cells (MCFCs) and solid oxide fuel cell (SOFCs). One of the well-known polymer electrolyte membranes in PEMFCs is the Nafion series developed by DuPont. The material has several

strengths in material properties, such as high chemical, thermal, and mechanical stability, and high proton conductivity. As such, Nafion may have wide applications in industry. However, the weaknesses of Nafion-series membranes include high cost, high fuel permeation (in the case of direct methanol fuel cells), and low proton conductivity at relatively high temperature above 90 °C, the temperature at which water is vaporized [1]. Because of such drawbacks in Nafion membranes, a number of alternative membranes based on hydrocarbon-type polymers have been studied. Poly(benziimidazole), poly(arylene ether sulfone), poly(arylene ether ketone), and polyimides are strong candidates, as these polymers are not only inherently stable with regard to thermal, chemical, and mechanical properties, but also easily sulfonated to provide proton conducting properties [2–12]. Many experimental data have shown that HC-based polymers can possibly overcome

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the weaknesses of Nafion membranes. Fuel crossover has been reduced substantially due to the creation of smaller ionic cluster dimensions than with Nafion membranes. Production costs are also competitive, because the raw materials are cheap, and the synthetic or sulfonation processes are relatively simple.

Despite the benefits, there are still some issues with HC membranes to be considered. As the conductivity is too low compared to Nafion at the same level of ion exchange capacity (IEC), a high degree of sulfonation is usually required to obtain a desired conductivity. At a high level of sulfonation, dimensional or mechanical failure associated with high water uptake is usually observed, especially at relatively high temperature. The membranes also become so brittle in a dry state that fabrication of MEAs with long-term interfacial stability is not feasible. Both Nafion membranes HC-based membranes show low conductivity at low humidity.

Our research group has recently studied the preparation of membranes based on sulfonated poly(ether ether ketone) [3,4,13–16]. This material is easily purchasable, cost competitive, easily sulfonated, and easily fabricated into membranes. Composite membrane systems are proposed to address same problems that arise with such hydrocarbon-based membranes. The composite membranes are established by accommodating phosphorous organosiloxane network and sulfonated mesoporous benzene silica into the sulfonated poly(ether ether ketone) base material. Organosiloxane network is a rubbery polymer synthesized from an inorganic siloxane-based compound and an organic compound containing phosphoric acid [17–20]. This polymer is not only mechanically tough and flexible, but electrochemically proton conductive, due to the presence of phosphoric acids. Its mechanical properties are expected to compensate for the brittleness of sPEEK membranes. Sulfonated mesoporous benzene silica is a type of periodic mesoporous material (PMO). When it possesses many hexagonal cylindrical mesopores that are 2–10 nm in diameter, the water imbibed by these mesopores is not easily vaporized from pores by capillary condensation effects [21–26]. The specific pore volume and specific surface area of PMO are very high, but still controllable to accommodate many water molecules. This PMO can be sulfonated to provide proton conductivity, allowing protons to be easily transported through the capillary pores in the presence of water. The role of sulfonated mesoporous benzene silica is to keep the water content at a high level to maintain high conductivity, even at low relative humidity.

We have synthesized each component of a composite membrane system separately, and used them to fabricate composite membranes by a solvent cast method. Essential membrane properties such as the proton conductivity, water uptake, methanol permeability, and thermal, mechanical, and dimensional stability were investigated. Attention was focused on the capillary condensation effect on the proton conductivity at low humidity. An MEA was fabricated with selected composite membranes to compare cell performance at low humidity.

## 2. Experimental

### 2.1. Materials

PEEK (ICI Company, Rotherham, UK, Mw 100,000 g mol<sup>-1</sup>), methylsulfonic acid (MSA) (Acros Organics, USA), N,N-dimethyl acetamide (DMAc) (Fluka Chemie AG), and sulfuric acid (Duksan Reagents & Chemicals, Korea) were used to synthesize sPEEK. Cetyltrimethylammonium chloride (CTAC) solution (25 wt%, Aldrich, St. Louis, MO, USA), 1,4-bis(triethoxysilyl)benzene (BTEB) (Aldrich), (3-mercaptopropyl)trimethoxysilane (MPTMS) (95 wt%, Aldrich), sodium hydroxide (99%, Duksan), hydrogen peroxide (30 wt%, Duksan), hydrochloric acid (37 wt%, Aldrich), and sulfuric

acid (Duksan) were used to prepare mesoporous benzene silica materials. 3-Glycidyloxypropyltrimethoxysilane (GPTMS) (TCI, Tokyo, Japan) and 1-hydroxyethane-1,1-diphosphonic acid (HEDPA) (TCI) were used to synthesize organosiloxane networks. Pt/C 40% (Alfa Aesar, Ward Hill, MA, USA), Nafion solution (5 wt%, DuPont, Wilmington, DE, USA), isopropyl alcohol (Aldrich), and carbon paper (CNL Energy, Korea) were used to prepare MEA.

### 2.2. Preparation of composite membranes

#### 2.2.1. Synthesis of sulfonated poly(ether ether ketone) (sPEEK)

PEEK was dried in a vacuum oven at 100 °C for at least 2 d. 20 g of dry PEEK was slowly dissolved in methylsulfonic acid (MSA) at 30 °C. When it was completely dissolved, 800 mL of sulfuric acid (97%) was added to start the sulfonation reaction. In this reaction, the concentration of PEEK solution was fixed at 5/100 (PEEK/sulfuric acid, w/v%). Sulfonation reaction was terminated by placing the reactor in an ice chamber. The sulfonated PEEK (sPEEK) was precipitated when the solution was poured into deionized (DI) water. The product was washed repeatedly with DI water until its pH was 6, and then dried in an oven at 60–100 °C for at least 1 d.

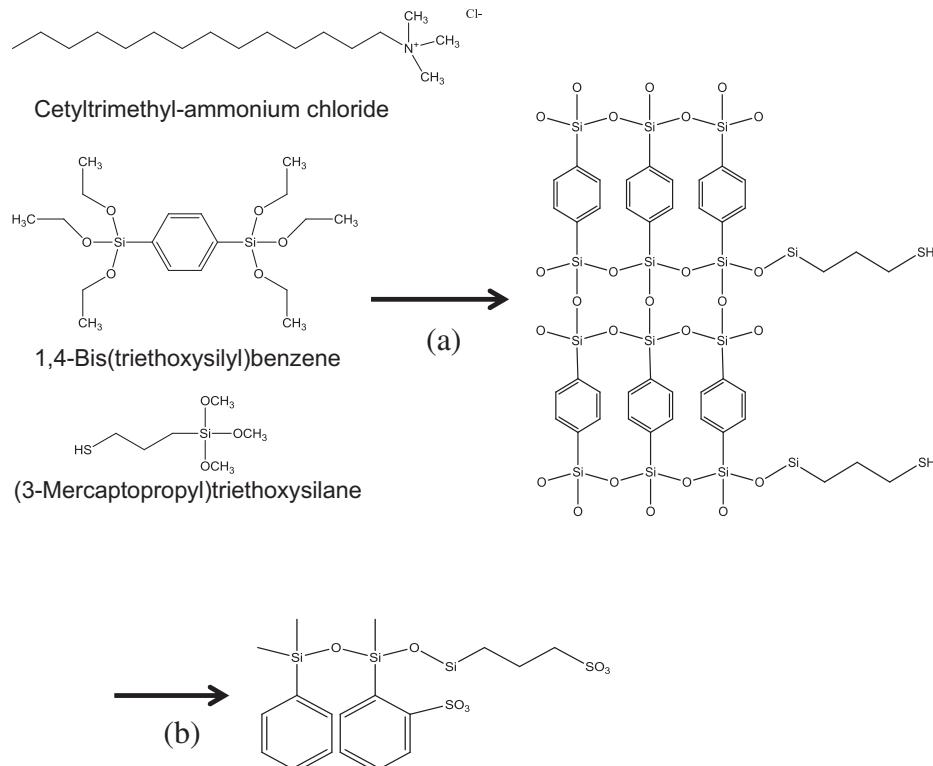
#### 2.2.2. Synthesis of sulfonated mesoporous benzene–silica (SMBS)

Mesoporous benzene–silica (MBS) was synthesized from CTAC as shown in Fig. 1(a). CTAC was dissolved in a mixture containing 22.38 g of DI water and 0.12 g of NaOH at room temperature. After agitation for 2 h, 1.04 g of BTEB and 0.73 g of MPTMS were added to the solution. The white precipitates were obtained after agitation for about 2 h, and kept at 100 °C for 24 h. The unreacted materials were washed out by stirring the precipitates in a mixture containing 75 mL of ethanol and 2 g of HCl at 70 °C for 12 h. The products were obtained after filtration and then further washed several times with DI water and acetone consecutively. The final product, MBS, was obtained after drying at 100 °C for 2 h. More details of the procedure for this MBS synthetic process are available elsewhere [26].

Benzene groups of MBS were first sulfonated. 1 g of MBS was placed in 500 mL of sulfuric acid (98%). After agitation for 3 h, the mixture was cooled down in 2 L of DI water for 12 h to obtain precipitates. The precipitates were washed with DI water and acetone several times. The Si group of MBS was then sulfonated. 10 g of hydrogen peroxide (30 wt%) was added to 0.3 g of the benzene sulfonated MBS particles. After the mixture was agitated at room temperature for 12 h, the product was filtrated and placed in 500 mL of 6 M sulfuric acid under agitation for 24 h. The final product was obtained after washing it in DI water and ethanol several times and then drying at 60 °C for 1 d. Fig. 1(b) shows the schematic sulfonation reaction of MBS.

#### 2.2.3. Preparation of composite membranes

0.95 g of GPTMS and 1.4 g of HEDPA were mixed with 5 g of DMAc, and 1 g of DI water, separately. After stirring each for 5 min, the two mixtures were combined with the GPTMS/HEDPA homogeneous solution. 0.3 g of the SPEEK sample obtained after sulfonation for 65 h (sPEEK65) was completely dissolved in 9.7 g of DMAc. 0.03 g of SMBS (10 wt % to sPEEK) was added and dispersed in sPEEK solution by magnetic stirring for 2 h, followed by sonication for 24 h. GPTMS/HEDPA solution prepared beforehand was mixed with the SMBS-dispersed sPEEK65 solution. The resulting mixture was mechanically agitated for 4 h and then sonicated for another 4 h. The final product was cast onto glass and then dried at 80 °C for 10 h, and then at 120 °C for 2 h in vacuum to prepare membranes. Fig. 2 shows the synthetic reaction of organosiloxane network structure from GPTMS and HEDPA.



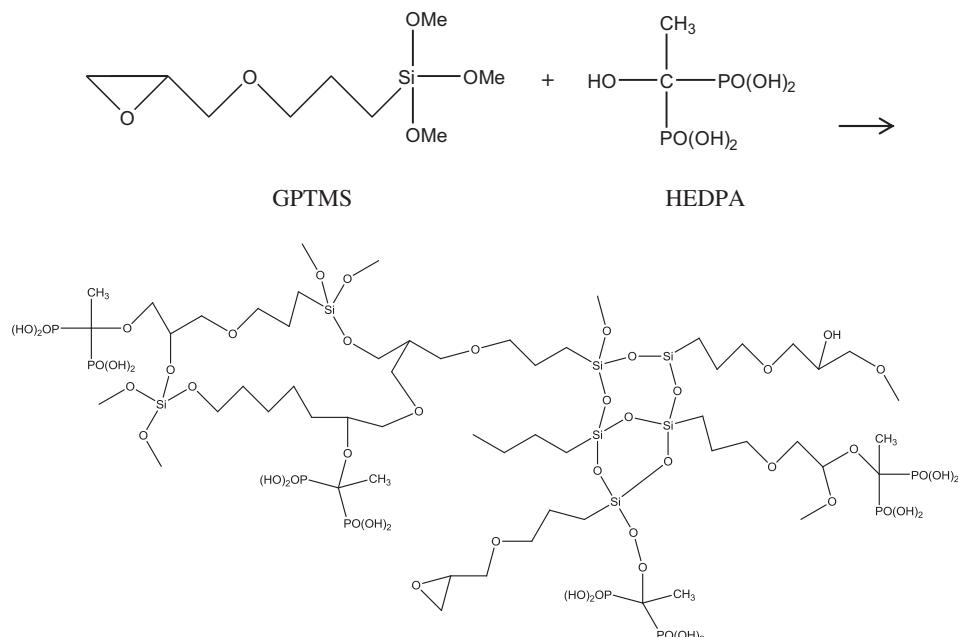
**Fig. 1.** Synthetic reactions of (a) MBS and (b) SMBS.

### 2.3. Characterization

#### 2.3.1. Chemical and physical structure

The chemical structure of sPEEK and SMBS were identified using a 500-MHz solid-state FT-NMR spectrometer (Unity Inova, Varian Technology, Palo Alto, CA, USA) and FT-IR spectrometer (Bruker iFs-66, Germany). The morphology of the SMBS was analyzed using FE-

TEM (JEM-2100F, JEOL, Tokyo, Japan) operated at an accelerated potential of 200 kV. For this analysis, SMBS particles were dispersed in ethanol at 1 mg mL<sup>-1</sup>, and loaded onto a copper grid to obtain a TEM image. The surface area and pore volume of the SMBS were determined according to the BET (Brunauer–Emmett–Teller) method using nitrogen adsorption–desorption isotherms measured on a Micromeritics 2020 analyzer operated at 77 K under



**Fig. 2.** Synthetic reaction of organosiloxane network structure from GPTMS and HEDPA.

N<sub>2</sub> atmosphere (ASAP 2420, Micromeritics Instrument Corporation, Atlanta, USA). The ionic cluster dimension of the membranes was analyzed using a Small Angle X-ray Scattering (SAXS) analyzer (Pohang accelerator laboratory in POSTECH, Korea). The wavelength of the synchrotron radiation beam was 1.608 Å. The distance between the sample and detector was fixed at 50 cm, and the beam exposure time to the sample was 120 s. The membrane sample was pretreated by placing it in a 1 M cesium solution for 24 h prior to each measurement. The scattering vector,  $q$ , was obtained from the following equation:

$$q = (4\pi/\lambda)\sin \theta \quad (1)$$

where  $\lambda$  is the wavelength of the radiation beam, and  $2\theta$  is the scattering angle.

The Bragg distance  $d$  is related to  $q$  as follows:

$$d = 2\pi/q \quad (2)$$

### 2.3.2. Ion exchange capacity (IEC) and degree of sulfonation (DS) of sPEEK

The IEC and DS of the sPEEK membranes prepared were determined using a back titration method. 0.1 g of SPEEK was placed in 200 mL of 0.05 N NaOH aqueous solution, and the mixture was stirred for 3 d. As the OH<sup>-</sup> concentration decreases continuously by the neutralization reaction between SPEEK and sodium hydroxide, the equilibrium OH<sup>-</sup> concentration could be determined by titration with 0.05 N HCl aqueous solution. The moles of OH<sup>-</sup> consumed are equivalent to the moles of SO<sub>3</sub>H<sup>+</sup> present in SPEEK samples. The pH of the solution was measured using a pH meter (SP-701, SUN-TEX, New Taipei City 221, Taiwan). More details of the procedure are available in a previous report [4].

### 2.3.3. Water uptake

Water uptake was determined by measuring the mass of the samples before and after the absorption of water. The samples were completely dried prior to water absorption. The sample was placed in a water bath, and its weight was measured periodically until no weight change was observed. The water uptake percentages were determined using the following equations:

$$\text{Water uptake \%} = \left( W_{\text{wet}} - W_{\text{dry}} \right) / W_{\text{dry}} \times 100 \quad (3)$$

where  $W_{\text{wet}}$  and  $W_{\text{dry}}$  are the weights of the sample in the wet and dry states.  $T_{\text{wet}}$  and  $T_{\text{dry}}$  are the thicknesses of the sample in the wet and dry states, respectively.

### 2.3.4. Proton conductivity

Impedance spectroscopy (IM6ex, ZAHNER Elektrik, Kronach, Germany) was employed to measure the proton conductivity of the composite membrane. The membrane was placed in a BEKK-TECH cell (BT-112 Conductivity Cell, BekkTech LLC, Loveland, CO, USA). Hydrogen gas was fed at 1 L min<sup>-1</sup>, and the measurements were conducted at 95% relative humidity (RH). The proton conductivity was calculated from the ohmic resistance  $R$ , as shown in equation (4).

$$\sigma = L/(R \times W \times T) \quad (4)$$

Here,  $L$  (=0.425 cm) is the distance between two electrodes in the BEKKTECH cell, and  $W$  and  $T$  are the width and thickness of the membrane, respectively.

### 2.3.5. Mechanical strength

The tensile properties of the membrane were measured using a universal tensile machine (UTM-model 5565, Lloyd, Fareham, UK). Samples were stored in water at room temperature before measurement. The sample dimensions were 10 mm ( $W$ ) × 40 mm ( $L$ ), and a 250 N load cell was used.

### 2.3.6. Cell performance

1 g of Pt/C (40 wt%), 12.45 g of Nafion® solution (5 wt%), 8.9 g of 2-propyl alcohol (IPA), and 1.6 g of DI water were mixed together, and the mixture was sonicated for 24 h to prepare a catalyst solution. The catalyst solution was coated onto the surface of the membrane by spraying it 3–4 times in 5-min intervals. The active area of the membrane for this process was 2.5 cm × 2.5 cm. A gas diffusion layer was loaded onto the catalyst-coated sPEEK membrane on both sides to fabricate a membrane electrode assembly (MEA). The fuel cell performance was measured using a PEM unit cell station provided by CNL Energy (SPPSN-300, CNL Energy, Korea). The flow rates of hydrogen and oxygen at the anode and cathode sides were 1.5 cm<sup>3</sup> min<sup>-1</sup> and 2.0 cm<sup>3</sup> min<sup>-1</sup>, respectively. The cell test was conducted at different RHs of 95%, 70%, and 45% at 100 °C.

## 3. Results and discussion

### 3.1. Sulfonation of PEEK

The sulfonation of PEEK was confirmed using FT-IR, and the results are shown in Fig. 3. New IR bands appear in the sPEEK IR spectrum at 705 cm<sup>-1</sup>, 1077 cm<sup>-1</sup>, 1022 cm<sup>-1</sup>, 1270 cm<sup>-1</sup>, and 1490 cm<sup>-1</sup>, originating from S—O, S=O, and O=S=O stretching and SO<sub>3</sub>H<sup>-</sup> vibration, respectively.

The ion exchange capacity (IEC) and the degree of sulfonation (DS) of sPEEK membranes were determined as a function of the sulfonation time. In Fig. 4, IEC and DS increase correspondingly with sulfonation time. The values of IEC and DS were 1.27, 1.48, 1.78, 1.90, 1.92, and 2.2, and 41, 48, 60, 65, 66, and 77% when the sulfonation reaction times were 15, 30, 45, 60, 75, and 90 h, respectively.

### 3.2. Synthesis of SMBS

In Fig. 5(a), the FT-IR spectra for MBS before and after sulfonation are shown for comparison. A new IR band appears at 1080 cm<sup>-1</sup> after sulfonation, which corresponds to the stretching of the O=S=O group. This confirms the sulfonation of MBS. <sup>13</sup>C NMR spectroscopy

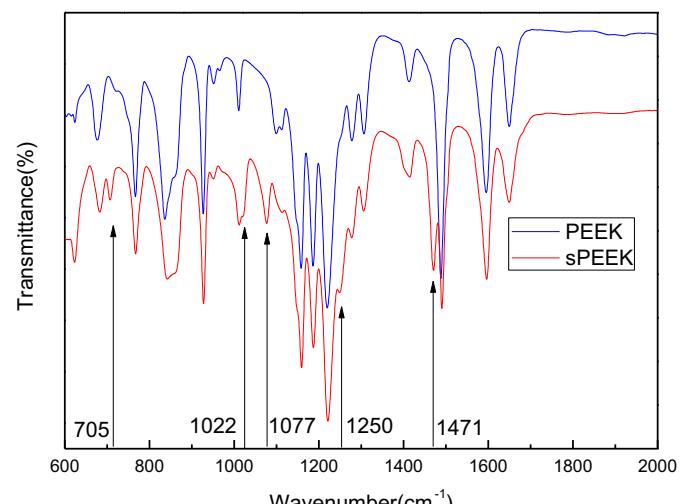


Fig. 3. FT-IR spectra of PEEK and sPEEK.

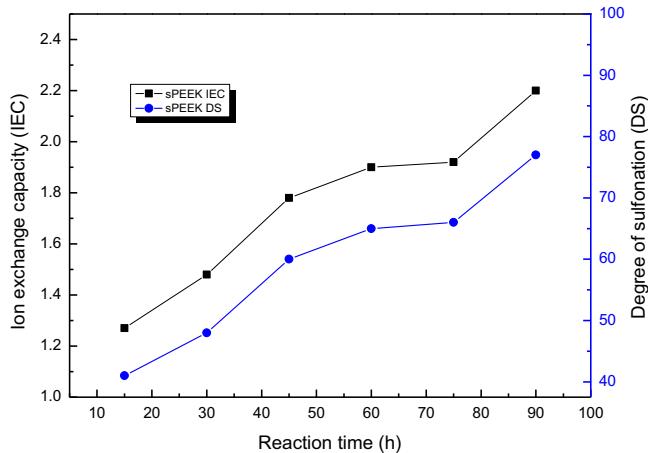


Fig. 4. Degree of sulfonation (DS) and Ion exchange capacity (IEC) of sPEEK membranes.

**Table 1**  
BET surface area and pore volume of SMBS.

Sample	Surface area, SBET ( $\text{m}^2 \text{ g}^{-1}$ )	Pore volume, $V_p (\text{cm}^3 \text{ g}^{-1})$	Pore diameter, $D_p (\text{nm})$
SMBS	670.78	0.57	3.17

was employed to investigate the sulfonation of MBS. The spectra for MBS and SMBS are illustrated in Fig. 5(b). In contrast to the NMR spectrum of MBS, a characteristic band at 50 ppm is observed for SMBS, arising from the proton in the  $\text{C}-\text{SO}_3\text{H}$  bond in SMBS.

In Table 1, the BET surface area of the synthesized SMBS is about  $670.78 \text{ m}^2 \text{ g}^{-1}$ , the total pore volume is  $0.57 \text{ cm}^3$ , and the pore diameter is 3.17 nm. Nitrogen adsorption and desorption isotherms are shown in Fig. 6(a), correspondingly. The pore diameter of the SMBS measured by BET analysis is supported by the TEM image and SAXS pattern in Fig. 6(b) and (c), respectively. Fig. 6(b) shows the ordered mesoporous structure with a hexagonal arrangement of cylindrical channels of the SMBS measured by TEM. In Fig. 6(c), a strong peak at  $0.15 \text{ \AA}^{-1}$  originates from the porous structure of SMBS, and its diameter was determined as 4.22 nm from its position using the Bragg equation.

### 3.3. Characterization of composite membranes

#### 3.3.1. sPEEK65/OSPN membranes

In Fig. 7(a–c), the water uptake, proton conductivity, and tensile strength of the sPEEK/OSPN membranes are illustrated according to their composition, respectively. The water uptake and proton conductivity increase with OSPN content, as OSPN possesses hydrophilic and proton-conductive phosphoric acid groups. The elongation significantly increases with OSPN content, while the tensile strength deceases slightly. This behavior is attributed to the flexibility and toughness properties of the OSPN component. Although the proton conductivity and flexibility increase with OSPN, the composite membranes containing more than 20% OSPN were not considered further, because of the excessive water uptake and insufficient tensile strength. Water uptake increases with temperature, but it was still less than 60% at  $100^\circ\text{C}$  with OSPN contents of up to 20%. The proton conductivity monotonically increases with temperature at 90% relative humidity. All membranes were mechanically stable in the hydrated state in this temperature range. Temperature dependence of proton conductivity of Nafion membranes is shown in Table 2 for comparison.

#### 3.3.2. sPEEK65/SMBS membranes

Fig. 8(a–c) shows the water uptake, proton conductivity, and mechanical properties of the sPEEK/SMBS composite membranes. The water uptake and proton conductivity increase with the SMBS concentration because the hydrophilicity and proton conductivity properties were aided by the sulfonated porous walls in SMBS conductors. The water uptake and proton conductivity also increased with temperature. The water uptake reaches about 55% at  $100^\circ\text{C}$  when the SMBS concentration is 20%. Although the proton conductivity increases with SMBS content, the mechanical strength is not positively affected by its introduction. Both the tensile strength and elongation decrease with increasing SMBS content. Composite membranes containing more than 20% SMBS content

**Table 2**  
Temperature dependence proton conductivity of Nafion membrane.

Temperature ( $^\circ\text{C}$ )	40	50	60	70	80	90
Ion conductivity ( $\text{S cm}^{-1}$ )	0.043	0.047	0.051	0.057	0.061	0.066

Temperature dependence proton conductivity of Nafion membrane.

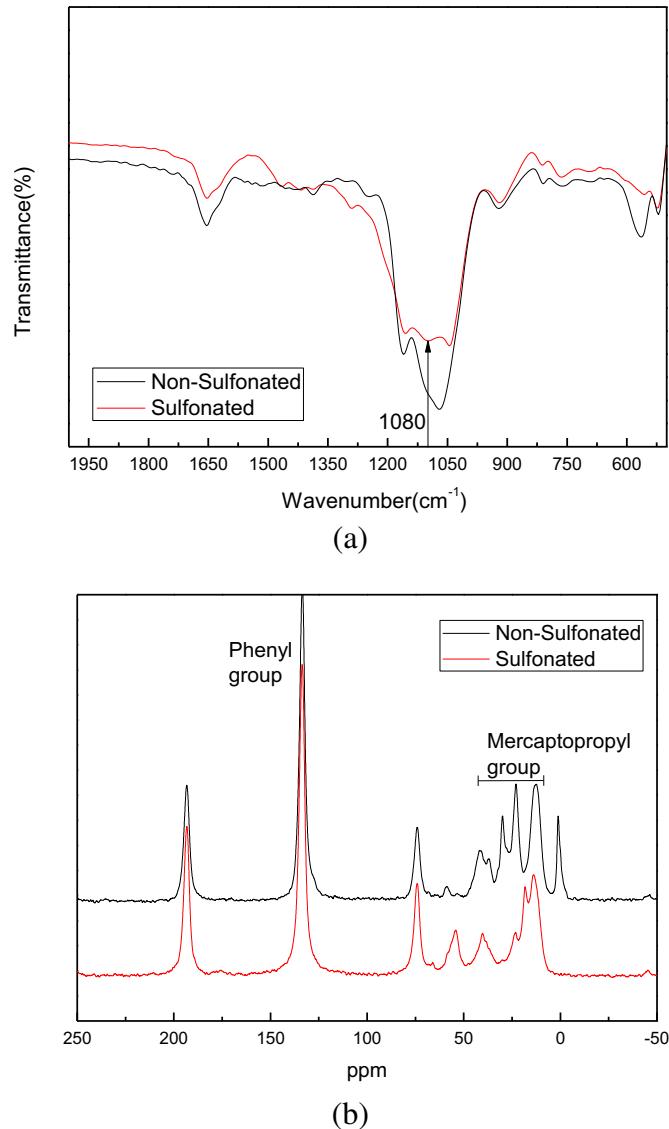
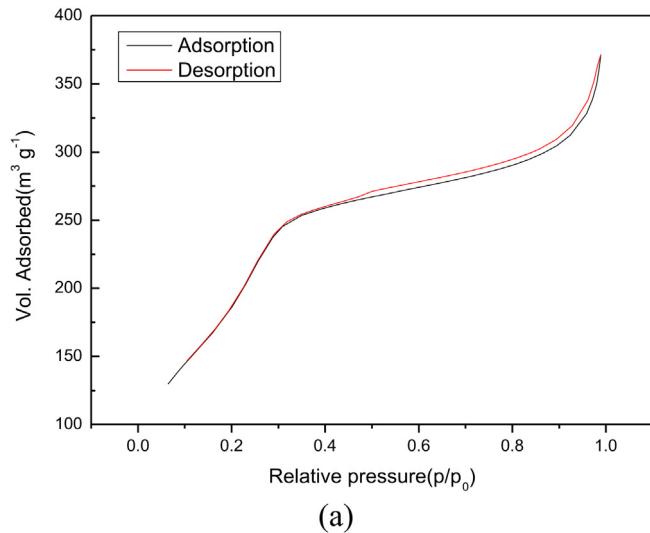
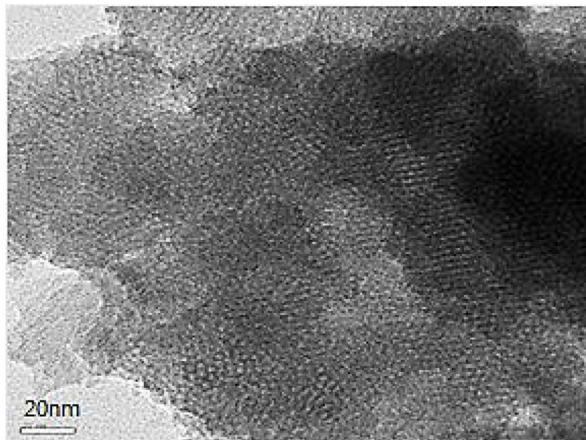


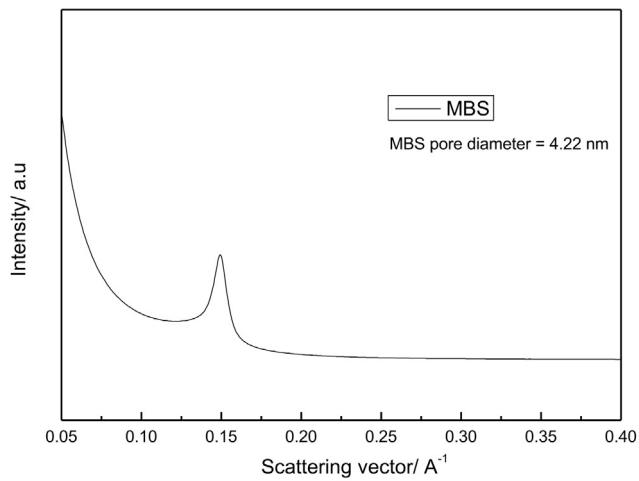
Fig. 5. (a) FT-IR spectra and (b) <sup>13</sup>C NMR spectra of MBS and SMBS.



(a)



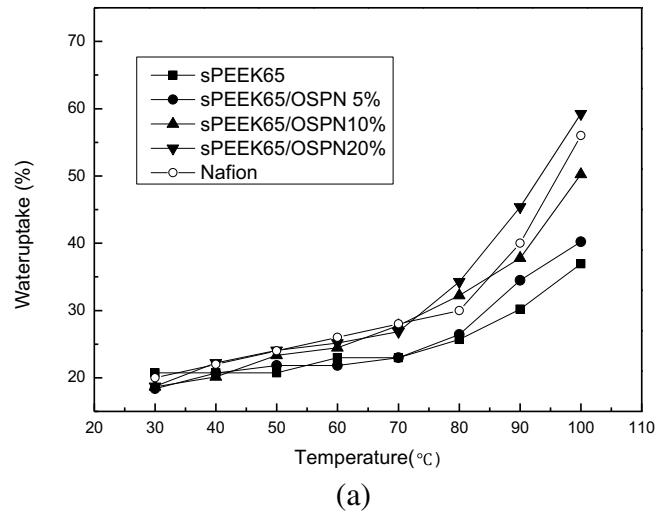
(b)



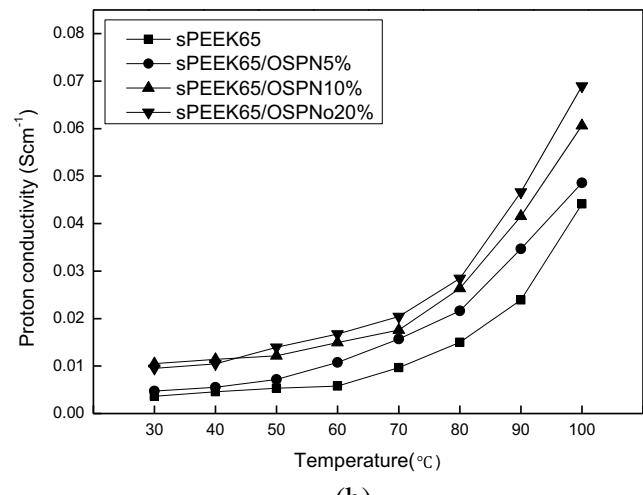
(c)

**Fig. 6.** (a) Nitrogen adsorption–desorption isotherms, (b) 2D-hexagonal cylindrical pore structure, and (c) SAXS patterns of the SMBS.

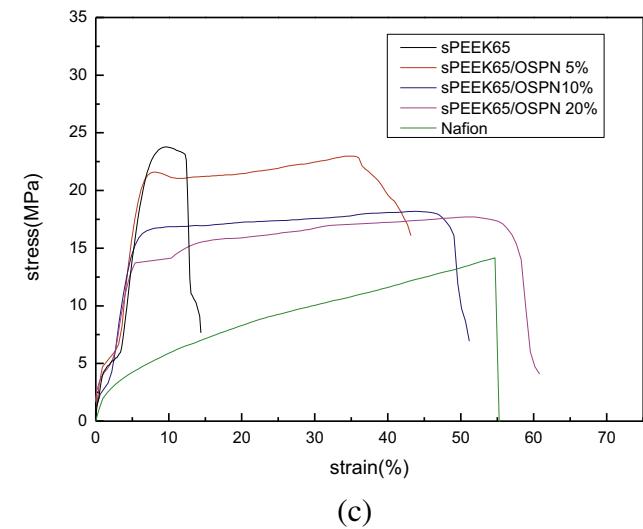
are not mechanically stable over long terms [27], so they were not prepared. The mechanical failure of the membranes containing more than 20% SMBS particles is presumably caused by the imperfect interfacial adhesion between the dispersed SMBS particles and the sPEEK matrix.



(a)



(b)

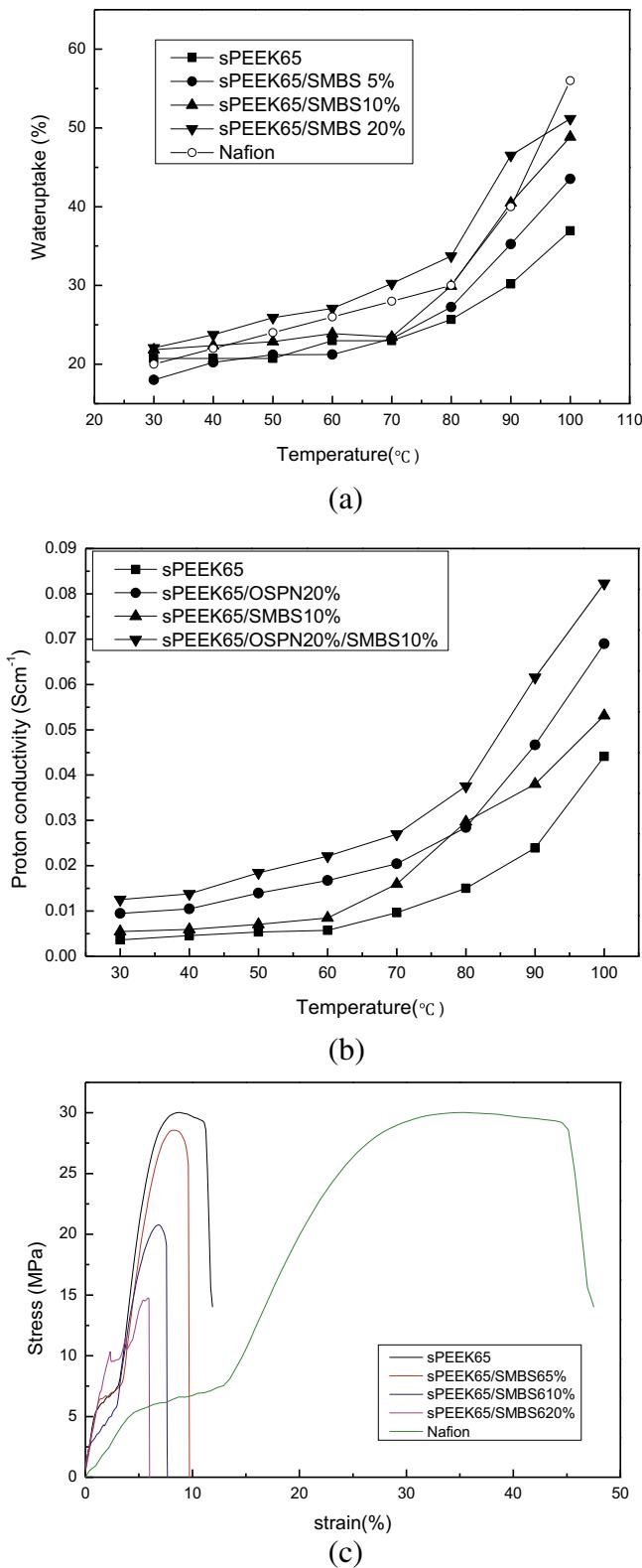


(c)

**Fig. 7.** (a) Water uptake, (b) proton conductivity, and (c) tensile properties of sPEEK65/OSPN composite membranes.

### 3.3.3. sPEEK65/OSPN/SMBS composite membranes

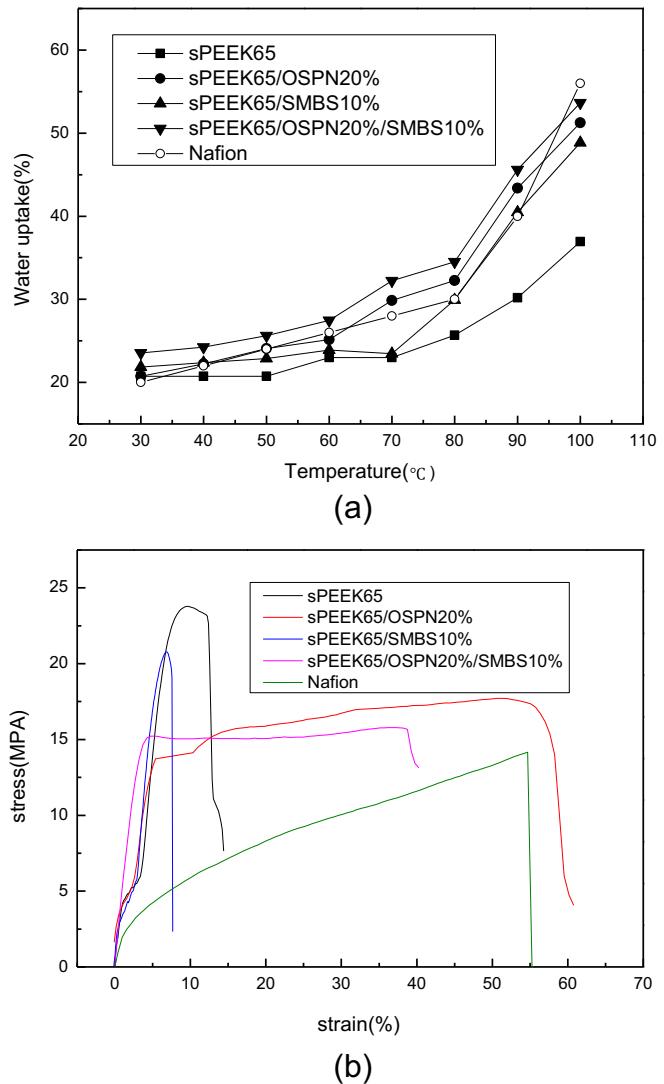
Although both OSPN and SMBS components enhanced the proton conductivity of sPEEK membranes similarly in the hydrated state, SMBS and OSPN have different effects on the other properties of the membranes. The OSPN increased the toughness



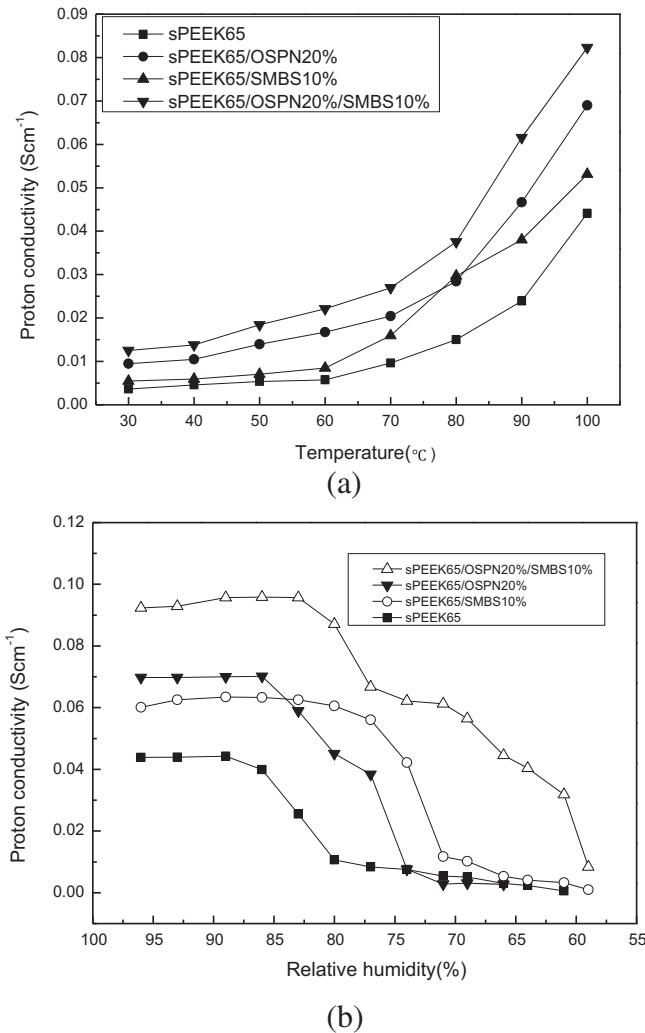
**Fig. 8.** (a) Water uptake, (b) proton conductivity, and (c) tensile properties of sPEEK65/SMBS composite membranes.

of the membranes, but the SMBS produced an opposite trend. However, SMBS may have a much more positive contribution than OSPN by the capillary condensation effect provided by its unique cylindrical porous structure. This anti-hydration effect may eventually lead to relatively high proton conductivity, even

at low humidity. Thus, we have prepared composite membrane systems composed of three components, sPEEK, OSPN, and SMBS, in order to investigate the effect of each component on the overall membrane properties, including the proton conductivity in both hydrated and dehydrated states, as well as the mechanical properties and water uptake. In these composite membranes, the composition of OSPN and SMBS was fixed at 20 and 10%, respectively, based on the properties determined for the sPEEK/OSPN and sPEEK/SMBS binary composite system membranes. The OSPN content of 20% was chosen because the water uptake was too high below this value, but above it, the tensile strength was too low, as shown in Fig. 7. The SMBS content of 10% was selected because the elongation upon breakage was too low when the content was greater, as shown from Fig. 8, despite the proton conductivity having monotonically increased. Fig. 9(a) and (b) respectively shows the water uptake and mechanical strength of the pristine sPEEK, sPEEK/OSPN, sPEEK/SMBS, and sPEEK/OSPN/SMBS membrane systems. While the introduction of OSPN and SMBS together enhances the water uptake somewhat more than with an OSPN or SMBS single-blended system, it was still lower than 55%, even temperatures as high as 100 °C. The loss of elongational resistance after the addition of the SMBS



**Fig. 9.** (a) Water uptake and (b) tensile properties of sPEEK65/OSPN/SMBS composite membranes.



**Fig. 10.** Proton conductivity of sPEEK65/OSPN/SMBS composite membranes (a) at different temperatures (relative humidity of 95%) and (b) at different relative humidities (100 °C).

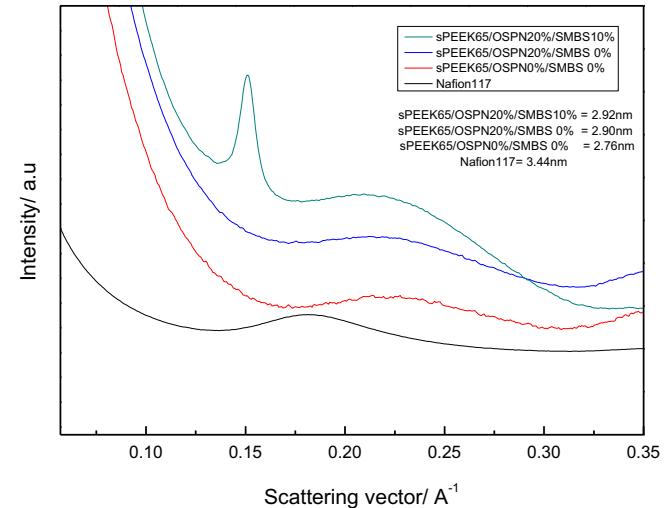
component was compensated for by the addition of the OSPN component, as shown in Fig. 9(b), while sustaining the tensile strength above 15 MPa.

The ternary component system enhances proton conductivity more than the binary system for the entire temperature range from room temperature to 100 °C, as shown in Fig. 10(a). The activation energy,  $E$  of composite membranes was determined from the Arrhenius type temperature dependence of conductivity in equation (5). It was determined from the slope of linear plot of  $\ln \sigma$  vs.  $\ln 1/T$  after linear regression.

$$\sigma = \sigma_0 \exp(-E/RT) \quad (5)$$

As shown in Table 3, the activation energy ranges from 7 J mol $^{-1}$  to 16 J mol $^{-1}$ .

The most striking effect of SMBS on the sPEEK/OSPN/SMBS membrane properties is the high proton conductivity at relatively



**Fig. 11.** SAXS patterns of composite membranes.

low humidity. Einsla et al. [28] reported a significant ion conductivity decrease for the Nafion membranes with the decrease of relative humidity. Fig. 10(b) shows the proton conductivity as a function of relative humidity at 100 °C. Compared to the pristine sPEEK membrane and sPEEK/OSPN membrane system, the addition of SMBS increases the proton conductivity significantly in the low humidity range. This was caused by the capillary condensation effect of 2-D hexagonal cylindrical mesopores in the SMBS proton conductors, which could keep water molecules inside the pores even in a low-humidity environment.

### 3.3.4. Ion cluster dimension of membranes

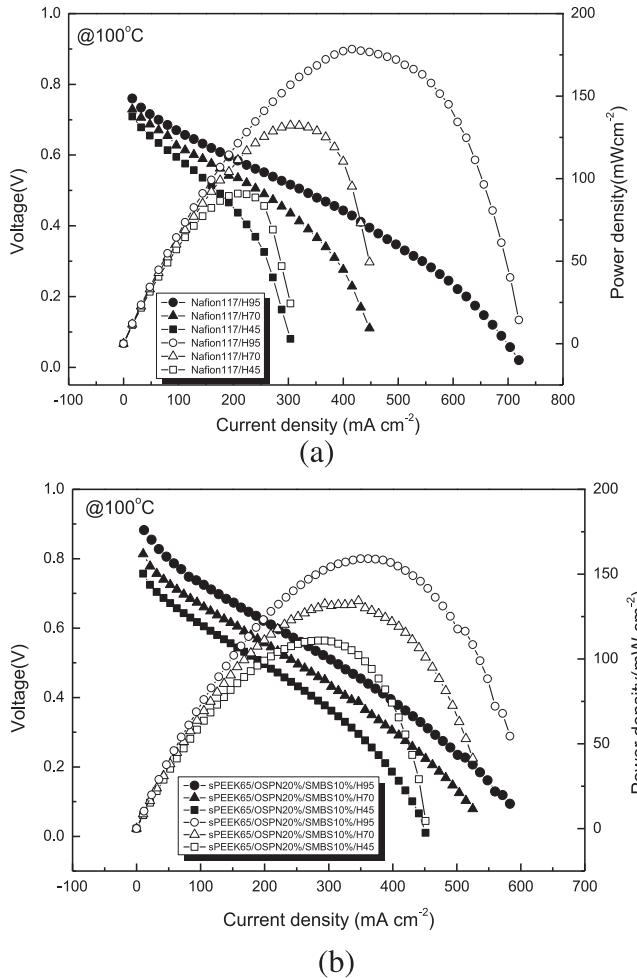
The properties of membranes, such as the proton conductivity, methanol permeability, and water uptake, are closely related to the phase separation structure of the membrane. The ion cluster dimension was characterized by SAXS analysis, and the results are shown in Fig. 11. The introduction of OSPN slightly increases the ion cluster dimension of the membrane from 2.76 nm to 2.9 nm due to the increase of hydrophilicity associated with the OSPN component. The introduction of SMBS had little effect on the band position at 0.225 Å $^{-1}$  originating from the matrix polymer membrane, and led to an additional band around 0.15 Å $^{-1}$  from the mesoporous structure of the SMBS conductors. This means that SMBS and the matrix polymer components do not affect the phase separation or pore structures of the other components by blending.

### 3.3.5. Cell performance

Fig. 12 shows the cell performance of the MEA fabricated with the composite membranes composed of 20% OSPN and 10% SMBS at different relative humidity and 100 °C. The cell performance decreased with decreasing relative humidity because of the dehydration effect of the membrane. In comparison to the Nafion-based MEA, however, there was very little reduction in the cell performance of the composite membrane-based MEA. While the maximum power of the composite membrane-based MEA was comparable to that of the Nafion-based one at 95% relative

**Table 3**  
Activation energy of sPEEK/OSPN/SMBS composite membrane.

Sample	sPEEK65	sPEEK65/OSPN5	sPEEK65/OSPN10	sPEEK65/OSPN20	sPEEK65/SMBS5	sPEEK65/SMBS10	sPEEK65/SMBS20	sPEEK65/OSPN20/SMBS10
Activation energy (J mol $^{-1}$ )	11.2	11.6	7.9	9.2	15.6	11.6	11.5	9.0



**Fig. 12.** PEMFC cell performance of (a) Nafion and (b) sPEEK65/OSPN/SMBS composite membranes at different relative humidities of 95, 70, and 45%, respectively.

humidity, it was much higher at low relative humidities such as 70% and 45%. The maintaining of such high cell performance was primarily attributed to the anti-dehydration effect of the membrane, by which water could be kept in the sulfonated mesopores of the SMBS component.

#### 4. Conclusion

SPEEK-based composite membranes containing OSPN and SMBS are prepared to enhance the elongational properties and proton conductivity in reduced humidity. While the brittleness of SPEEK is modified by the formation of semi-IPN structure with OSPN, the low-proton-conductivity SPEEK membrane in low humidity is improved by the addition of SMBS particles. The proton conductivity increases with the introduction of OSPN and SMBS, while maintaining the water uptake below 60%, even at temperatures as high as 100 °C. Compared to the pristine SPEEK membranes, the ternary component composite membranes result in an increase in

the elongation upon breaking by about 10 times. The SAXS patterns of the composite membranes explain the water-related properties of the composite membranes. While the introduction of the OSPN component slightly increases the ion cluster dimension of the membrane from 2.76 nm to 2.9 nm by the formation of IPN structure, the introduction of SMBS has little effect on the ion clusters dimension of the matrix polymer membrane, but leads to additional 3-nm cluster domains associated with its mesoporous structure. The maximum power of the composite membrane-based MEA is comparable to that of the Nafion based one, at 95% relative humidity, but is higher at low relative humidities such as 70% and 45%, due to the capillary condensation effect of the SMBS component arising from the 2-D hexagonal cylindrical mesopores with sulfonated walls.

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